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Laundering Variables in Removing Carbaryl and Atrazine Residues from Contaminated Fabrics

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During mixing and application of pesticides, the clothing worn by agricultural or urban pesticide applicators is subject to contamination. Completeness of pesticide removal in laundering is essential if the garment is to be used again. Henry (1980) has documented that fabrics commonly used for work clothing, such as cotton and/or polyester, will continue to be worn by midwestern farmers when handling and applying chemicals. Although moisture-resistant protective clothing is available for pesticide mixer-handlers and applicators, factors such as thermal and psychological comfort, cost, availability and lack of appreciation for the need precludes widespread use of protective apparel systems. Dermal exposure may occur from inadequately laundered garments which had been contaminated with pesticides. Thus, refurbishment is an essential and critical part of continued safety.

The Federal Task Group on Occupational Exposure to Pesticides requires that all protective clothing be thoroughly washed after each day's work. Soil release from textile substrates is a complex phenomenon and is affected by the chemical nature of the pesticide soil, the textile fiber and applied finish. It also depends upon the fiber, yarn and fabric geometries, as well as the laundering variables. A study by Keaschall et al. (1986) established that laundering effectiveness varied among pesticide classes. Organochlorine insecticides had the largest percent of pesticide residue remaining after laundering. Carbamates showed the smallest percentage of pesticide residue, and organophosphates fell in between the other two classes. However, these researchers found differences both among and within pesticide classes. Finley et al. (1974) reported that laundering reduced the residue level of contaminated fabrics, and that DDT, methylparathion, and toxaphene residues were differentially removed. Easter and DeJonge (1985) reported that pesticide formulation played a major role in controlling decontamination. They included fabric variations as well and found that captan in a wettable powder formulation was more difficult to remove from heavy-weight denim fabric than from chambray, Tyvek® and

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Goretex®. Easley et al. (1981, 1982a,b) and Laughlin et al. (1985) showed that methylparathion emulsifiable concentrate formulation was more difficult to remove than a wettable powder or encapsulated formulation.

Raheel and Gitz (1985) established that absorbency and wicking characteristics of fabrics are influenced by fiber, yarn and fabric geometries. Pesticide solutions wicked through fabrics with tightly twisted yarns more quickly than those with loosely twisted yarns. Others (Kim et al. 1982, 1986) have shown that tight twisting of yarns or tight packing into fabrics can prevent wash liquors from removing penetrated pesticides. Obendorf et al. (1982) and Solbrig et al. (1985) have shown that fiber content in fabrics plays an important role, and that laundering released pesticide residue more completely from polyester fibers, while cotton retained pesticide residue in the lumen and convolutions of the fiber.

Multiple launderings have been found to be more effective in removing methylparathion residues from contaminated fabrics (Finley et al. 1979; Easley et al. 1982b; Easter 1985). Finley et al. (1979) reported that as the amount of pesticide in fabrics increased, washing became less effective. A cold wash (30°C) removed significantly less pesticide than a 49°C and 60°C wash (Easley et al. 1982b; Laughlin et al. 1985; Lillie et al. 1981).

This study examines the efficacy of laundering variables such as detergent type, wash water temperature and number of launderings in removal of carbaryl (1-Naphthyl-N-methyl carbamate) and atrazine (2-Chloro-4-ethylamino-6-isopropylamino-S-triazine) residues from fabrics of various fiber contents. In addition, the effect of durable-press functional finish on residue removal from polyester/cotton fabrics is examined.

MATERIALS AND METHODS

A factorial design experiment with 3 replications was developed. The factors included 9 fabrics, 2 pesticides, 2 pesticide formulations, 2 laundering temperatures, 2 detergent types and 3 repeat launderings.

Statistical differences in after-laundry residue attributable to fiber content, finish, pesticide type and formulation, as well as laundering variables were calculated using a General Linear Model Analysis of Variance (ANOVA) with an indication of significance at the $p \leq 0.05$ level. Separation of means was achieved with Least Significant Means, and the Duncan's Multiple Range Test.

Fabrics were obtained from Testfabrics, Inc., Middlesex, NJ, except for the spunbonded olefin fabric which was contributed by E.I. du Pont Co. Fabric characteristics are described in Table 1. Fabrics were initially stripped of warp sizing and manufacturer-applied fabric softeners by washing them as per AATCC Test Method 135-1978, R-82 (1983). Fabric specimens were prepared according to ASTM D1682-64, R-75 (1983) and cut to 8 x 8 cm sample size.

Table 1. Fabric characteristics

Fabrics	Fabric weight (g/m^2)	Yarns per cm W	Yarns per cm F	Yarn no. (Tex) W	Yarn no. (Tex) F	Yarn twist (Turns/cm) W	Yarn twist (Turns/cm) F
						Singles	
100% Cotton #407 poplin	222	44	23	25	41	7.0	5.0
50/50 PET[a]/Cotton #7428 poplin	200	44	20	30	24	7.0	5.0
65/35 PET/Cotton #7402 poplin	178	41	23	22	28	7.0	5.0
100% Polyester #767 plain weave	116	25	19	29	20	8.0	7.0
						2-Ply	
100% Nylon #361 spun nylon 66 type 200 plain weave	149	21	23	40	23	6.0	8.0
100% Acrylic #864 spun orlon 75 plain weave	141	19	15	37	36	5.0	5.0
100% Olefin Spunbonded (Tyvek®)	40						

[a]PET = Polyester

Two pesticides were used for contaminating the fabrics: carbaryl, in wettable powder (Sevin 50 W) and flowable liquid (Sevin® 4L) formulation, and atrazine, also in wettable powder (Aatrex® 80 W) and flowable liquid (Aatrex® 4 LC) formulation.

Fabric specimens were placed horizontally over platforms consisting of widely spaced wires, thus providing support but very few contact points. Two hundred µL of 1.25% (a.i) pesticide solution was pipetted in the central area of the fabric specimen using a programmable micropipette. The contaminated fabrics were air-dried for 12-14 hours at 20 ± 1°C and 65% relative humidity. Two sets of fabric specimens were contaminated, one set was laundered for after-laundry residue analysis and the other set served as the control for making paired comparisons and validation of baseline pesticide extraction efficiency.

The contaminated specimens were individually laundered in stainless steel canisters of an Atlas Launder-Ometer using 150 mL of a 0.2% detergent solution, a 9-min wash cycle and two rinse cycles of 5 and 3 min each. Twenty-five steel balls per canister provided agitation during laundering. Distilled water was used for both laundering and rinsing at either 49°C or 60°C. Two types of detergents, a 6.1% phosphate powder detergent (Tide®) and a nonionic heavy duty liquid detergent (Dynamo®), were evaluated for their pesticide soil removal efficacy. The specimens were laundered once, twice or three times.

The unlaundered control, as well as the laundered fabric specimens were individually extracted in three 50 mL aliquots of reagent grade acetone. Each fabric specimen with solvent was shaken for 45 min on a mechanical shaker at 280 rpm and decanted. The process was repeated, and the three aliquots were combined. The unlaundered contaminated fabrics established a baseline to determine the pesticide recovery rate, which was used to calculate after-laundry pesticide residues.

Residue analysis was done by gas chromatography using technical grade carbaryl (99.8% a.i.) and atrazine (99.9% a.i.) as external standards. A Hewlett Packard 5790A gas chromatographer with an electron capture detector was used and data were recorded using the HP 3390A data integrator. Separation was achieved on a 2 m x 2 mm glass column packed with 3% SP-2100 on 100/120 mesh size supelcoport. The carrier gas was nitrogen at a flowrate of 25 ml/min. Injection, oven and detector temperatures were 250°C, 180°C (raised to 250°C after 1 min) and 300°C, respectively. The average of 9 values per fabric type, per laundering condition, was analyzed and expressed in micrograms per square centimeter ($\mu g/cm^2$) of the contaminated fabric.

RESULTS AND DISCUSSION

Significant differences were not found due to pesticide formulations (wettable powder vs. flowable liquid) in after-laundry residue retention of fabrics. Therefore, pooled data for wettable powder and flowable liquid formulations are presented and discussed.

Fabric variables included fiber content and the presence or absence of durable-press (DP) finish on polyester/cotton blend fabrics. Fiber content in general did not influence after-laundry residue retention (Table 2). Although differences in residue retention were noted, they were not statistically significant. Compared to other fabrics, after one laundering cycle, nylon fabric retained the highest amount of carbaryl residue, followed by cotton fabric and then polyester/cotton blend fabrics. The level of pesticide residue found in cotton and cotton-containing fabrics supports the electron microscopic work of Obendorf (1982) and Solbrig (1985) who postulated that the pesticides became trapped in the lumen, convolutions and crenulations of cotton fiber making it more difficult to remove

Table 2. Effect of fiber content on pesticide residue retention after one laundry ($\mu g/cm^2$)[a]

	Pesticide					
	Carbaryl			Atrazine		
Fabrics	Initial residue	After laundry	% removed	Initial residue	After laundry	% removed
100% Cotton	17.23	.119	99.5	35.65	.119	99.7
50/50 PET/Cotton	16.12	.035	99.8	31.61	ND[c]	100
65/35 PET/Cotton	23.52	.103	99.6	41.70	.309	99.5
100% Polyester	23.82	.071	99.7	49.63	ND	100
100% Nylon	19.64	.255	98.7	51.15	ND	100
100% Acrylic	13.34	.061	99.6	38.41	ND	100
100% Olefin (Spunbonded)	6.80[b]	.049	99.3	25.68	ND	100
	F-ratio = 1.02 NS[d]			F-ratio = 0.90 NS		

[a]Average of 9 values from 3 specimens in each of the 3 replications.
[b]Excess rolled off after 30 minutes.
[c]ND = not detected; [d]NS = not significant at $p \geq .05$.

than is true of removal from smooth fibers. However, this does not explain the higher residue level of carbaryl in nylon fabric observed after one laundry cycle in this study. It is hypothesized that the chemical affinity of -C=O in carbaryl with the -NH of the polyamide chains on the surface layers of the nylon fiber may be responsible for adsorption of carbaryl and reduced level of release in laundering.

With atrazine, only cotton and polyester/cotton blend fabrics exhibited slight residue retention after laundering, supporting the work of Obendorf (1982) and Solbrig (1985). However, the differences in residue retention were not statistically significant.

Durable press finished 50/50 and 65/35 polyester/cotton fabrics retained more pesticide residue than unfinished polyester/cotton fabrics (Table 3); however, the differences were not statistically significant ($p \leq 0.05$).

Contaminated fabrics were laundered once, twice and three times. One laundering cycle removed more than 96% of carbaryl residue from all fabrics (Table 4). No significant difference was found

Table 3. Effect of fabric finish on after-laundry residue retention

Fabrics	Pesticide residue μg/cm² Carbaryl Initial residue	Carbaryl After laundry	Atrazine Initial residue	Atrazine After laundry
50/50 Polyester/Cotton				
UN[a]	16.1	0.03	31.6	0.29
DP[b]	15.8	0.18	30.6	0.08
65/35 Polyester/Cotton				
UN	23.8	0.05	41.7	ND[c]
DP	15.6	0.08	35.6	ND
	F-ratio=0.32 NS[d]		F-ratio=0.47 NS	

[a]UN = unfinished; [b]DP = durable press; [c]ND = not detected; [d]NS = not significant at $p \leq 0.05$.

Table 4. Mean percent carbaryl removed after one laundry at 49°C and 60°C

Fabrics	Heavy duty liquid detergent (Dynamo®) 49°C wash	Heavy duty liquid detergent (Dynamo®) 60°C wash	Powder detergent (Phosphate, Tide®) 49°C wash	Powder detergent (Phosphate, Tide®) 60°C wash
100% Cotton	99.4[a]	99.6[a]	99.5[a]	99.9[a]
50/50 PET/Cotton	99.9[a]	99.9[a]	99.8[a]	99.8[a]
50/50 PET/Cotton + DP	98.8[ab]	99.0[a]	96.4[b]	97.1[b]
65/35 PET/Cotton	99.8[a]	99.9[a]	99.6[a]	99.9[a]
65/35 PET/Cotton + DP	99.5[a]	99.9[a]	96.0[b]	97.6[b]
100% Polyester	99.8[a]	100[a]	99.7[a]	99.9[a]
100% Nylon	97.9[b]	99.9[a]	98.7[ab]	99.9[a]
100% Acrylic	99.9[a]	100[a]	99.6[a]	100[a]
100% Olefin (Spunbonded)	100[a]	100[a]	99.6[a]	100[a]

Mean followed by the same letter within treatments are not significantly different at $p \leq 0.05$.

between wettable powder and flowable liquid formulations. Almost all carbaryl residue was removed after the second laundry and no residue was detected after the third laundry cycle. One laundering cycle removed atrazine almost completely, both in wettable powder as well as flowable liquid formulation (Table 5). Atrazine was formulated as an ammonium salt, and was highly water soluble, hence the ease of removal in laundering.

Wash water temperature of 49°C was as effective as 60°C in removing both pesticides (Tables 4 and 5). In comparing the efficacy of the nonionic heavy duty liquid detergent (HDL) with the phosphate powder detergent, significant difference was detected. It is interesting to note that after laundering with powder detergent (Tide®) only 96% of the carbaryl (Table 4) and 98.1% of atrazine (Table 5) was removed from 65/35 polyester/cotton fabric which had DP finish, as opposed to 99% or higher pesticide residue removal from all other fabrics in powder or HDL detergent. These results support the findings of Laughlin et al. (1985), that HDL detergent is more effective in removing either oil-based pesticide formulation, or pesticide residues from oleophilic surfaces such as DP finished polyester/cotton fabrics.

Table 5. Mean percent atrazine removed after one laundry at 49°C and 60°C

Fabrics	Heavy duty liquid detergent (Dynamo®)		Powder detergent (Phosphate, Tide®)	
	49°C wash	60°C wash	49°C wash	60°C wash
100% Cotton	99.4[a]	99.6[a]	99.7[a]	99.8[a]
50/50 PET/Cotton	99.7[a]	100[a]	100[a]	99.9[a]
50/50 PET/Cotton + DP	99.1[a]	100[a]	100[a]	100[a]
65/35 PET/Cotton	100[a]	100[a]	98.2[b]	99.6[a]
65/35 PET/Cotton + DP	100[a]	100[a]	98.1[b]	99.2[a]
100% Polyester	100[a]	100[a]	100[a]	100[a]
100% Nylon	100[a]	100[a]	100[a]	100[a]
100% Acrylic	100[a]	100[a]	100[a]	100[a]
100% Olefin (Spunbonded)	100[a]	100[a]	100[a]	100[a]

Mean followed by the same letter within treatments are not significantly different at $p \leq 0.05$.

Thus, carbaryl and atrazine in wettable powder and flowable liquid formulations are readily removed from contaminated fabrics under commonly used laundering regimen. Atrazine formulated as an ammonium salt is highly water soluble and is almost completely removed in one laundering, whereas carbaryl residue removal may take at least two repeat launderings. Warm wash water temperature (49°C) was found to be as effective in residue removal as hot (60°C) water for both pesticides. A statistically significant difference was found between the efficacy of HDL and powder detergent. Heavy duty liquid detergent was found to be more effective in removing pesticide residues from DP finished polyester/cotton fabrics commonly used for work apparel.

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